# CCCLVI.—*A Contribution to the Chemistry of Nitroso-compounds.*

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THE remarkable ease with which nitroso-compounds are reduced to hydroxylamino-derivatives by cold dilute hydriodic acid at the ordinary temperature (Earl and Kenner, J., 1927, 2139) has led us to consider the reaction more closely. It is well known that nitroso-chlorides, if not polymerised, are usually oximes, and even in those cases in which a polymeride of the true nitrosochloride is known, *e.g.*, pinol nitrosochloride, it can be changed into the *iso*nitroso-modification. Further, no indication has been found that the reaction is reversible, and, in the case of the oximes themselves, it is only comparatively recently that any evidence of a reversion to the nitroso-form has been obtained (Griffiths and Ingold, J., 1925, **127**, 1698). It is true that the tautomerism of *p*-nitrosophenol involves such a reversal, but this is due to the general inclination of quinonoid compounds to assume the more saturated benzenoid condition :
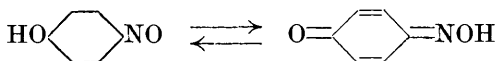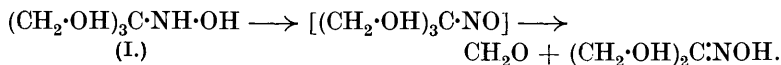

In these cases the change to the oximino-form is intramolecular, but the same tendency appears in intermolecular reactions. The facility with which *p*-nitrosodimethylaniline is converted into *p*-nitrosophenol by hydrolysis is perhaps the most familiar instance of this kind, and the reduction of nitroso-compounds to hydroxyl-amines by hydriodic acid is a reaction governed by the same tendency. In our view, it is best formulated as an additive reaction in the first place, followed by displacement of the iodine atom by hydrogen :
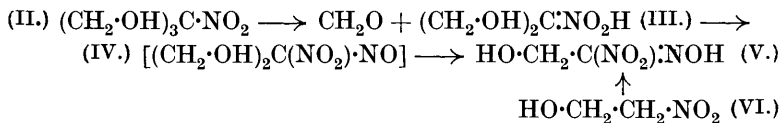
$$X \cdot N{:}O + HI \longrightarrow X \cdot NI \cdot OH \xrightarrow{\text{HI}} X \cdot NH \cdot OH + I_2.$$

The formation of N-hydroxyamidines from nitrosobenzene and methyleneanilines (Burkhardt, Lapworth, and Robinson, J., 1925, **127**, 2234) is also to be included under this heading :

$$Ar \cdot N:O + Ar' \cdot N:CH_2 \longrightarrow Ar \cdot N(OH) \cdot CH:NAr'.$$
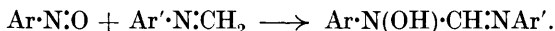
This brief review throws new light on the classical synthesis of glycerol by Piloty and Ruff (*Ber.*, 1897, **30**, 1656). This depends on the elimination of formaldehyde, which occurs when the hydroxyl-aminobutanetriol (I) is subjected to oxidation by yellow mercuric oxide. Clearly the reaction is only another illustration of the property of the nitroso-group just discussed :

$$(CH_2 \cdot OH)_3 C \cdot NH \cdot OH \longrightarrow [(CH_2 \cdot OH)_3 C \cdot NO] \longrightarrow$$
$$\text{(I.)} \qquad\qquad\qquad CH_2O + (CH_2 \cdot OH)_2 C:NOH.$$

The corresponding nitrobutanetriol (II) is itself stable, but also loses formaldehyde under the influence of alkali (Schmidt and Wilkendorf, *Ber.*, 1919, **52**, 389). Wilkendorf and Trénel (*Ber.*, 1923, **56**, 611) were, however, unable to accomplish the direct elimination of a second molecule of formaldehyde from the nitro-butanetriol. But the foregoing considerations make it clear that this must occur if a nitroso-group be appropriately introduced into the molecule of β-nitropropane-αγ-diol (III).

$$\text{(II.)} \ (CH_2 \cdot OH)_3 C \cdot NO_2 \longrightarrow CH_2O + (CH_2 \cdot OH)_2 C:NO_2H \ \text{(III.)} \longrightarrow$$
$$\text{(IV.)} \ [(CH_2 \cdot OH)_2 C(NO_2) \cdot NO] \longrightarrow HO \cdot CH_2 \cdot C(NO_2):NOH \ \text{(V.)}$$
$$\uparrow$$
$$HO \cdot CH_2 \cdot CH_2 \cdot NO_2 \ \text{(VI.)}$$

This prediction has been experimentally verified by treatment of the sodium salt of the diol with nitrous acid under precisely those conditions prescribed by V. Meyer and Constam (*Annalen*, 1882, **214**, 328) for the preparation of ethylnitrolic acid from nitroethane. The action of nitrous acid on the cooled aqueous solution of the salt at first causes the production of the characteristic well-known blue colour indicative of the formation of the pseudonitrol (IV), but this almost at once gives place in the alkaline solution to the red colour of the nitrolic acid salt. The formaldehyde produced has been identified by its condensation with β-naphthol, and the β-*hydroxyethylnitrolic acid* (V) has been isolated in the crystalline condition, and its constitution also established by its identity with the product obtained in the usual manner from β-nitroethyl alcohol (VI). Since, however, the sodium salt of β-nitropropane-αγ-diol is obtainable in one operation from nitromethane and formaldehyde (Wilkendorf and Trénel, *loc. cit.*), whereas nitroethyl alcohol has to be prepared from glycolchlorohydrin through the

iodohydrin and, as we found, then requires further purification through its sodium salt for the present purpose, the new reaction is the more convenient method of obtaining the acid. In order to demonstrate the general character of the reaction, we have also shown that ethylnitrolic acid is produced by the action of nitrous acid on the sodium salt of β-nitropropanol :

$$CH_3 \cdot C(CH_2 \cdot OH)\!:\!NO_2Na \longrightarrow CH_3 \cdot C(NO_2)\!:\!NOH + CH_2O.$$
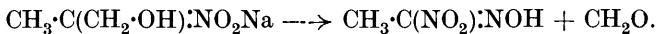
These reactions indicate that when the carbon atom next the nitroso-group does not carry a hydrogen atom which would enable the change, indicated in (VII), to the oximino-condition to occur,
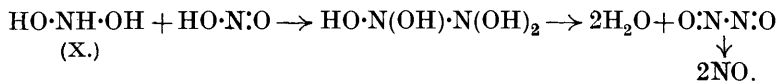

(VII.)   (VIII.)   (IX.)
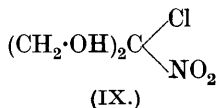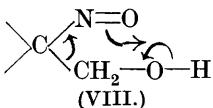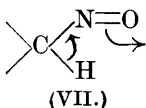
a methylol group can supply the necessary hydrogen atom, as shown by (VIII). In this case the electronic changes induced by the nitroso-group are transmitted through a chain of singly linked atoms. The same applies to the case of the nitrobutanetriol (II) and the fact that β-chloro-β-nitropropane-αγ-diol (IX) suffers elimination of formaldehyde rather than elimination of chlorine (Wilkendorf and Trénel, *loc. cit.*) illustrates the readiness with which such transmission occurs.

A number of other well-known reactions appear to depend on the characteristic of the nitroso-group emphasised above. For instance, the exceptional behaviour of nitrous acid in so readily forming an anhydride can be ascribed to the following reactions :

$$HO \cdot N\!:\!O + H \cdot ON\!:\!O \longrightarrow HO \cdot N\!\!<^{OH}_{ON\!:\!O} \longrightarrow H_2O + O\!:\!N \cdot O \cdot N\!:\!O.$$
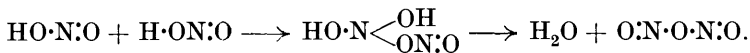
Similarly, the almost instantaneous esterification of ethyl alcohol by cold dilute nitrous acid (compare Thiele and Eichwede, *Annalen*, 1900, **311**, 366, footnote) and the course of the well-known reactions between potassium nitrite and potassium hydrogen sulphite (Raschig, *Annalen*, 1887, **241**, 207) are readily understood from this point of view. Again, the interaction of hydriodic acid and nitrous acid would, according to the scheme already suggested for nitroso-compounds in general, lead to the compound (X), which could then

$$HO \cdot NH \cdot OH + HO \cdot N\!:\!O \longrightarrow HO \cdot N(OH) \cdot N(OH)_2 \longrightarrow 2H_2O + O\!:\!N \cdot N\!:\!O$$
$$\text{(X.)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$
$$2\dot{N}O.$$

react with more nitrous acid in the manner indicated, resulting in the eventual formation of nitric oxide.

Again, nitrous acid probably derives its distinctive value as a reagent for reactive methylene groups from its tendency to form an oximino-derivative (compare Wolff, *Annalen*, 1895, **288**, 10) :

$$\text{-CH}_2 \longrightarrow \text{-CH·N(OH)}_2 \longrightarrow \text{-C:NOH} + H_2O.$$
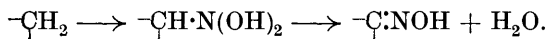
It does not seem previously to have been realised that, owing to the correspondence in chemical relationships of the CH group with the nitrogen atom and of the imino-group with the oxygen atom, a close constitutional connexion exists between methyl alcohol, hydroxylamine, and hydrogen peroxide, and, in fact, each undergoes catalytic dehydrogenation by platinum-black. Extending now Wieland's formulation in the cases of methyl alcohol and hydrogen peroxide (*Ber.*, 1921, **54**, 2353) to that of hydroxylamine, we have :

$$\text{H·N}{<}^{\text{H}}_{\text{OH}} \longrightarrow H_2 + \text{HN:O.}$$
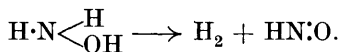
Actually ammonia, water, and nitrous oxide are formed (Tanatar, *Z. physikal. Chem.*, 1902, **40**, 475). Apparently nascent hydrogen and a part of the " nitroxyl " first formed give rise to ammonia, whilst the remainder is converted into nitrous oxide :

$$2\text{HNO} \longrightarrow \text{HN(OH)·N:O} \longrightarrow \text{N:N:O.}$$

This gas is produced quantitatively by oxidation of hydroxylamine with ferric sulphate (Raschig, *Annalen*, 1887, **241**, 188; *Z. anorg. Chem.*, 1904, **17**, 1411) as well as by reduction of nitrous acid (Raschig, *Z. anorg. Chem.*, 1904, **17**, 1398) and, particularly interesting for the present discussion, by hydrolysis of nitrososulphonic acid (compare Abegg, " Handbuch der Anorganischen Chemie," 3, iii, 153) :

$$\text{O:N·SO}_3\text{H} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{HN:O.}$$
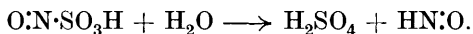
In the previous paper (Earl and Kenner, *loc. cit.*) it was pointed out that in spite of the well-recognised analogy between the carbonyl and the nitroso-group, the former does not undergo reduction with cold dilute hydriodic acid. This corresponds with the greater stability of the ketonic than the enolic form of simple carbonyl compounds, and the foregoing considerations would therefore lead

$$(\text{XI.}) \quad {>}\text{C}{<}^{\text{CH}_2\text{·OH}}_{\text{CHO}} \qquad (\text{CH}_2\text{·OH})_3\text{C·CHO} \quad (\text{XII.})$$

$$(\text{XIII.}) \quad \text{CH}_3\text{·C(CH}_2\text{·OH)}_2\text{·CHO} \qquad \text{CHMe}_2\text{·C(CH}_2\text{·OH)}_2\text{·CHO} \quad (\text{XIV.})$$

us to anticipate that the grouping (XI) would be stable and not lose formaldehyde under ordinary conditions. Accordingly penta-

erythrose (XII) (McLeod, *Amer. Chem. J.*, 1907, **37**, 20), αα-dimethylolpropanal (XIII) (Koch and Zerner, *Monatsh.*, 1901, **22**, 448), and αα-dimethylol-β-methylbutanal (XIV) (Lichtenstern, *ibid.*, 1905, **26**, 499) have been described and satisfactorily identified. On the other hand, Rave and Tollens showed that when pentaerythritol is oxidised by dilute nitric acid one of the products is an aldehyde of the empirical formula $C_4H_6O_3$, to which they assigned the constitution $CHO \cdot CH_2 \cdot O \cdot CH_2 \cdot CHO$ (*Annalen*, 1893, **276**, 65). In our view, the present discussion makes it practically certain that the course of the reaction is to be represented as follows :

$$(CH_2 \cdot OH)_4 C \longrightarrow (CH_2 \cdot OH)_2 C {<}^{CHO}_{CHO} \longrightarrow CH_2 O + HO \cdot CH_2 \cdot C {<}^{CHO}_{CH \cdot OH}$$

But our preliminary experiments to verify this hypothesis have shown that the task of preparing the dialdehyde in any quantity is likely to be laborious, since our yield of the characteristic bisphenylhydrazone described by Rave and Tollens was exceedingly small.

The difference between the nitroso- and the carbonyl group illustrated by these various reactions is one of degree, and is attributable to the fact that the nitrogen atom is more nearly equal to the oxygen atom than is the carbon atom in its tendency to acquire electrons. A system, therefore, in which nitrogen and oxygen atoms compete for four electrons is less likely to be stable than a similar one in which carbon occupies the place of nitrogen.

EXPERIMENTAL.

The solutions of sodium nitrite and potassium hydroxide employed in the following experiments contained respectively 64 g. and 53·6 g. in 120 c.c., as recommended by Meyer and Constam (*loc. cit.*).

β-*Hydroxyethylnitrolic Acid* (V).—Demuth and V. Meyer (*Annalen*, 1890, **256**, 43) were unable to obtain this compound either from β-nitroethyl alcohol or from the sodium salt, the preparation of which serves as a means of purifying the alcohol obtained by the usual method from glycoliodohydrin. Although the nitroethyl alcohol employed in our work was carefully purified by distillation at 101°/15 mm. (corr.) (compare Henry, *Rec. trav. chim.*, 1898, **17**, 2), we also were unable to isolate the nitrolic acid in experiments conducted under exactly the same conditions (the amount of alkali used was, however, three times as great in order to convert the nitro-compound into its salt) as those applied to the sodium salt in the manner now to be described.

β-Nitroethyl alcohol (13 g.) was converted into its sodium salt by treatment with a solution of sodium (3·3 g.) in alcohol (90 c.c.).

A solution of the sodium salt (11·4 g.) in water (5 c.c.), aqueous sodium nitrite (17 c.c.), and potassium hydroxide solution (5·6 c.c.), having been gradually acidified between − 10° and 0° with dilute sulphuric acid (5N), was again rendered alkaline and, after a few moments, re-acidified (compare Meyer and Constam, *loc. cit.*; Wieland, *Annalen*, 1907, **353**, 82). The solution was then rapidly filtered from sodium sulphate and extracted three times with cooled purified ether. Finally, the extract (40 c.c.), having been washed in a little ice-water and dried over sodium sulphate, was evaporated in a vacuum desiccator, first over sulphuric acid and then over phosphoric oxide. Crystallisation set in after 1 hour, when almost the whole of the ether had been removed, and the pure *nitrolic acid* (4 g.), m. p. 76—77° (decomp.; corr.), was obtained (Found : N, 23·2. $C_2H_4O_4N_2$ requires N, 23·3%). The poor yield (33%) was due to the solubility of the acid in water and to the undesirability of increasing the volume of ethereal extract and consequently delaying isolation of the product. It could be crystallised from solution in the minimum volume of dry ether by addition of three volumes of light petroleum, but gradually decomposed with evolution of nitrous fumes, even in a vacuum desiccator.

When an exactly similar experiment was performed with an equimolecular proportion of the sodium salt of β-nitropropane-αγ-diol (Wilkendorf and Trénel, *loc. cit.*) each addition of sulphuric acid was followed by the appearance of a temporary blue coloration, which rapidly changed to red. The product, m. p. 76—77° (decomp.) (Found : N, 22·9, 23·2%), did not depress the melting point of the specimen of β-hydroxyethylnitrolic acid obtained from β-nitroethyl alcohol. In order satisfactorily to demonstrate the production of formaldehyde in the reaction, it was necessary to examine the aqueous liquors under conditions which would avoid as far as possible decomposition of unextracted nitrolic acid into glycollic acid, and also to separate the formaldehyde from any of this acid which might nevertheless be produced. The liquors were therefore at once shaken with an excess of calcium carbonate at the ordinary temperature and the formaldehyde was removed by distillation after 24 hours. The distillate, which reduced Tollens's solution, was treated with β-naphthol in presence of hydrochloric acid, and furnished methylenedi-β-naphthol which, alone or mixed with an authentic specimen, melted at 206° (corr.).

Ethylnitrolic Acid from β-*Nitropropanol.*—A solution of sodium (5·7 g.) in methyl alcohol (40 c.c.) was very slowly added to a vigorously stirred solution of nitroethane (16 g.) and paraformaldehyde (6·6 g.) in methyl alcohol (120 c.c.). Owing to its solubility in methyl alcohol, the yield of the *sodium* salt of β-nitropropanol

(Found : N, 11·3; Na, 18·1.* $C_3H_6O_3NNa$ requires N, 11·0; Na, 18·1%) which separated from the solution was only 50%.

From the sodium salt (3·4 g.) and sodium nitrite (5 c.c.) and potassium hydroxide (1·7 c.c.) solutions, by the procedure already detailed in the case of nitroethyl alcohol, ethylnitrolic acid (2·7 g.), m. p. 84—85° (decomp.; corr.), was obtained. It was identified by analysis (Found : N, 26·6. Calc. for $C_2H_4O_3N_2$: N, 26·9%) and by direct comparison with a specimen, m. p. 85° (decomp.; corr.), prepared from nitroethane. The aqueous liquor from the preparation furnished a distillate in which formaldehyde was identified by condensation with β-naphthol; the methylenedi-β-naphthol obtained melted at 206° (corr.).

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